Project ID: ES299

June 6, 2017

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Microstructure Characterization and Modeling for Improved Electrode Design

Principal Investigator: Kandler Smith for Ahmad Pesaran*

Team: Francois Usseglio-Viretta, Peter Graf, S. Santhanagopalan (NREL)
Koffi (Pierre) Yao, Daniel Abraham, Dennis Dees, Andy Jansen (ANL)
Partha Mukherjee, Aashutosh Mistry, Ankit Verma (TAMU)

* Presently on detail with Vehicle Technologies Office

Project Title: Computer-Aided Battery Engineering Consortium

Awarded in response to FY15 VTO Lab Call

Project Leader
NREL, Kandler Smith

Task 1 Computational Efficiency
PI: Shriram Santhanagopalan

- **Cell/Electrode Making**
  ANL, Daniel Abraham, Koffi (Pierre) Yao, Dennis Dees

Task 2 Mechanical ECT Models
PI: Shriram Santhanagopalan

- **Material Characterization**
  OSU, Amos Gilat
- **Abuse Testing**
  SNL, Joshua Lamb
- **Cell/Module Fabrication**
  ANL, Daniel Abraham
- **Integration with ANSYS and LS-DYNA,**
  FST, Kelly Carnie **, GMU,** Paul Dubois

Task 3 Microstructure Modeling
PI: Kandler Smith

- **Microstructure Modeling**
  TAMU, Partha Mukherjee
- **Fabrication/Testing**
  ANL, Daniel Abraham, Koffi (Pierre) Yao

ES298, *Previous presentation*

ES299, *This Presentation*

ANL: Argonne National Laboratory
TAMU: Texas A&M University

Overview of Task 3: Microstructure Modeling

Timeline

- Project start date: Oct. 2016
- Project end date: Sept. 2018
- Percent complete: 45%

Barriers

- Long prototype-driven design cycle for lithium (Li)-ion batteries
- Electrode design models lack predictive capability due to tunable parameters
- Low cost, thick electrodes suffer from poor rate capability and Li plating

Budget

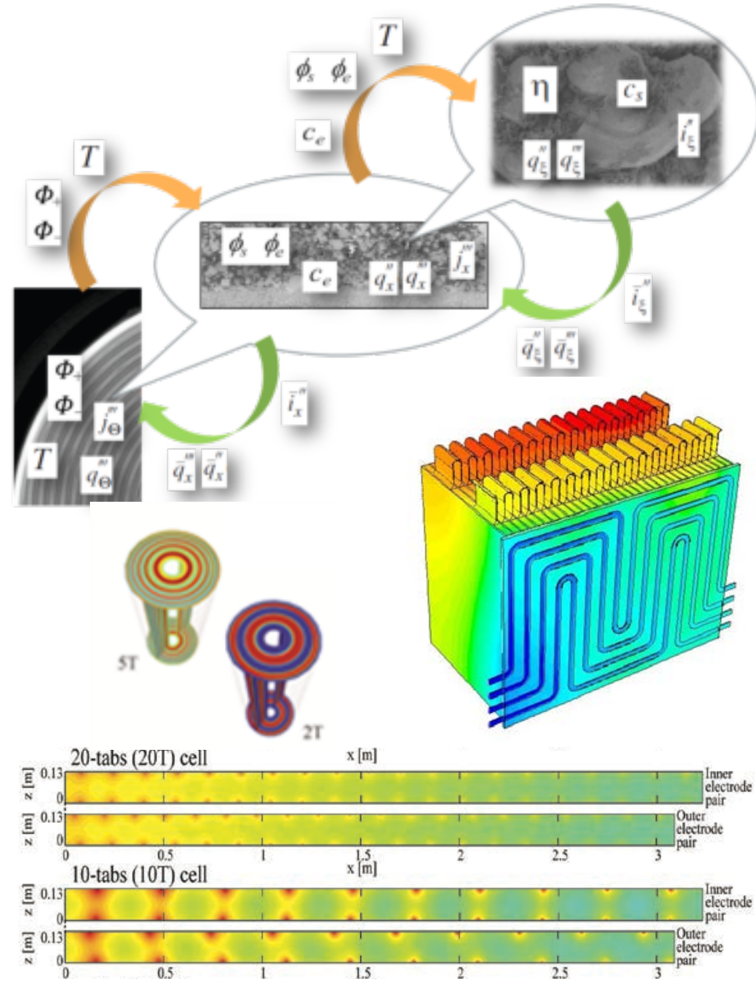
- Microstructure project funding: \$1.65M/3 yr.
  - DOE share: 100%
- Funding in FY 2016: \$550k
- Funding for FY 2017: \$550k

Partners

- Project lead: National Renewable Energy Laboratory (NREL)
- Collaborators:
  - Argonne National Laboratory (ANL)
  - Texas A&M University (TAMU)
  - University College London (UCL)

Background and Motivation

- VTO launched the Computer-Aided Engineering of Batteries (CAEBAT) project to develop validated modeling tools to accelerate development of batteries, in support of vehicle electrification R&D to reduce dependence on imported oil.
- Over 40 different end users from the community have adapted the Multi-Scale Multi-Domain (MSMD) modeling approach developed under CAEBAT.
- Feedback from the first few sets of end-users has helped us identify priorities that will enable wider use of model-based design:
    - Standardize identification of the model parameters
    - Increase computational efficiency
    - Extend the models to include mechanical failure of cells and packaging components
    - Close gaps between materials R&D and CAEBAT modeling tools

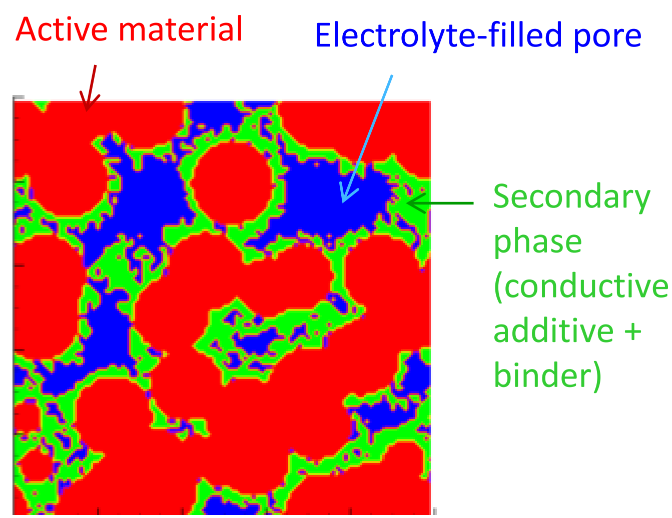


MSMD models previously developed in CAEBAT have been widely adapted in the community and helped us identify gaps.

Relevance – Objectives for March 2016 – March 2017

Electrode design through meso-scale modeling:

- Formulate meso-scale models that predict the impact of electrode recipe and design on performance
- Quantify effective properties used in electrode design models (e.g., surface area, diffusion length, tortuosity, role of inert secondary phase)



Example meso-scale model geometry of porous electrode

*A. Mistry & P. Mukherjee, TAMU

Microstructure characterization:

- Plan and initiate electrochemical, scanning electron microscopy (SEM), and tomography experiments to characterize and validate microstructure properties across relevant length scales

Microstructure modeling:

- Perform homogenization calculations to determine effective properties
- Initiate electrochemical direct numerical simulation (DNS) on detailed microstructure geometries from computed tomography (CT)

Impact: By making disruptive CAE design tools available on desktop computers for use by the battery community, this effort supports the following goals identified by the VTO:

1. Expedite path to $ 125/kWh electric vehicle (EV) battery costs by drastically reducing the number and duration of battery design cycles in the industry
2. Provide physical insights to optimize thick electrode designs for low cost, high energy density cells with reliable high rate performance

Milestones

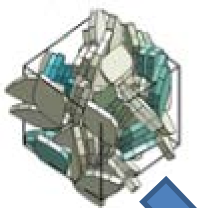
	Milestone Name/Description	Deadline	Milestone Type	Status
Task 3 - Microstructure Modeling	M.3.1 Document microstructure model formulation and validation plan	12/31/2015	Qrt. Prog. Meas.	Done
	M 3.2 Present microstructure project update at AMR	4/30/2017	Qrt. Prog. Meas.	On track
	M 3.3 Comparison of microstructural model simulations from both stochastic reconstructed (simulated) and tomographic (measured) geometries	9/30/2017	Qrt. Prog. Meas. **(Go/No-Go)**	On track
	M 3.4 Validation of electrode microstructure design tool for multiple electrode designs showing < 10% error between models and data	9/30/2018	Annual SMART	On track

SMART: Specific, Measurable, Attainable, Relevant, and Time-based

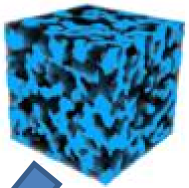
Approach

TEXAS A&M UNIVERSITY

Stochastic reconstruction & meso-scale physics



Validation of virtual 3D geometry



UCL

Argonne NATIONAL LABORATORY

Electrode fabrication, tomographic measurement, electrochemical response

Electrochemical performance validated for multiple designs

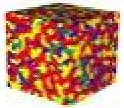
Design inputs

- Chemistry
- Morphology
- Size distribution
- Binder
- Conductive additive
- Calendaring

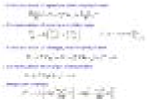
Microstructure Model

NREL NATIONAL RENEWABLE ENERGY LABORATORY

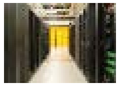
- Geometry



- Physics



- High Performance Computing (HPC)



Homogenization

Linkage to CAEBAT macroscopic simulation toolsets

Image credits:
Microstructure – Partha Mukherjee, TAMU
HPC – NREL image gallery
Coated electrode – hirano-tec.co.jp

Approach – Leveraging Electrode Library from CAMP Facility

Cathodes

NCM523 Positive Electrodes:
90 wt% Toda $Li_{1.03}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{0.97}O_2$
5 wt% C45 (Timcal)
5 wt% PVdF binder (Solvay 5130)
REFERENCE A-C015A CALENDARED
9.17 mg/cm^2 coating density
8.25 mg/cm^2 oxide density
33.5% electrode porosity
34-µm-thick composite coating
20-µm-thick Al current collector

UNCALENDARED		
LN2487-113-9	LN2487-113-10	LN2487-113-13
22.6 mg/cm^2 coating density	27.39 mg/cm^2 coating density	33.09 mg/cm^2 coating density
20.40 mg/cm^2 oxide density	24.65 mg/cm^2 oxide density	29.78 mg/cm^2 oxide density
47.4% electrode porosity	51.8% electrode porosity	49.1% electrode porosity
106-µm-thick composite coating	140-µm-thick composite coating	160-µm-thick composite coating
20-µm-thick Al current collector	20-µm-thick Al current collector	20-µm-thick Al current collector
CALENDARED		
36.6% electrode porosity	37.5% electrode porosity	36.8% electrode porosity
88-µm-thick composite coating	108-µm-thick composite coating	129-µm-thick composite coating

Anodes

A12 Graphite Negative Electrodes
Negative Electrode:
91.8 %wt ConocoPhillips: CGP-A12 graphite
2 wt% C45 (Timcal) + 0.17 %wt Oxalic Acid
6%wt KF-9300 Kureha PVDF binder
REFERENCE A002A CALENDARED
5.88 mg/cm^2 loading density - coating
5.51 mg/cm^2 active loading (A12 graphite + C45)
38.4% electrode porosity
44-µm-thick composite coating
10-µm-thick Cu current collector

UNCALENDARED		
LN3024-126-2	LN3024-126-4	LN3024-126-5
14.7 mg/cm^2 coating density	18.08 mg/cm^2 coating density	21.89 mg/cm^2 coating density
13.5 mg/cm^{2}A12 graphite density	16.6 mg/cm^{2}A12 graphite density	20.1 mg/cm^{2}A12 graphite density
51.4% electrode porosity	51.8% electrode porosity	50.7% electrode porosity
140-µm-thick composite coating	173-µm-thick composite coating	205-µm-thick composite coating
20-µm-thick Al current collector	20-µm-thick Al current collector	20-µm-thick Al current collector
CALENDARED		
38.0% electrode porosity	36.3% electrode porosity	38.8% electrode porosity
120-µm-thick composite coating	141-µm-thick composite coating	175-µm-thick composite coating

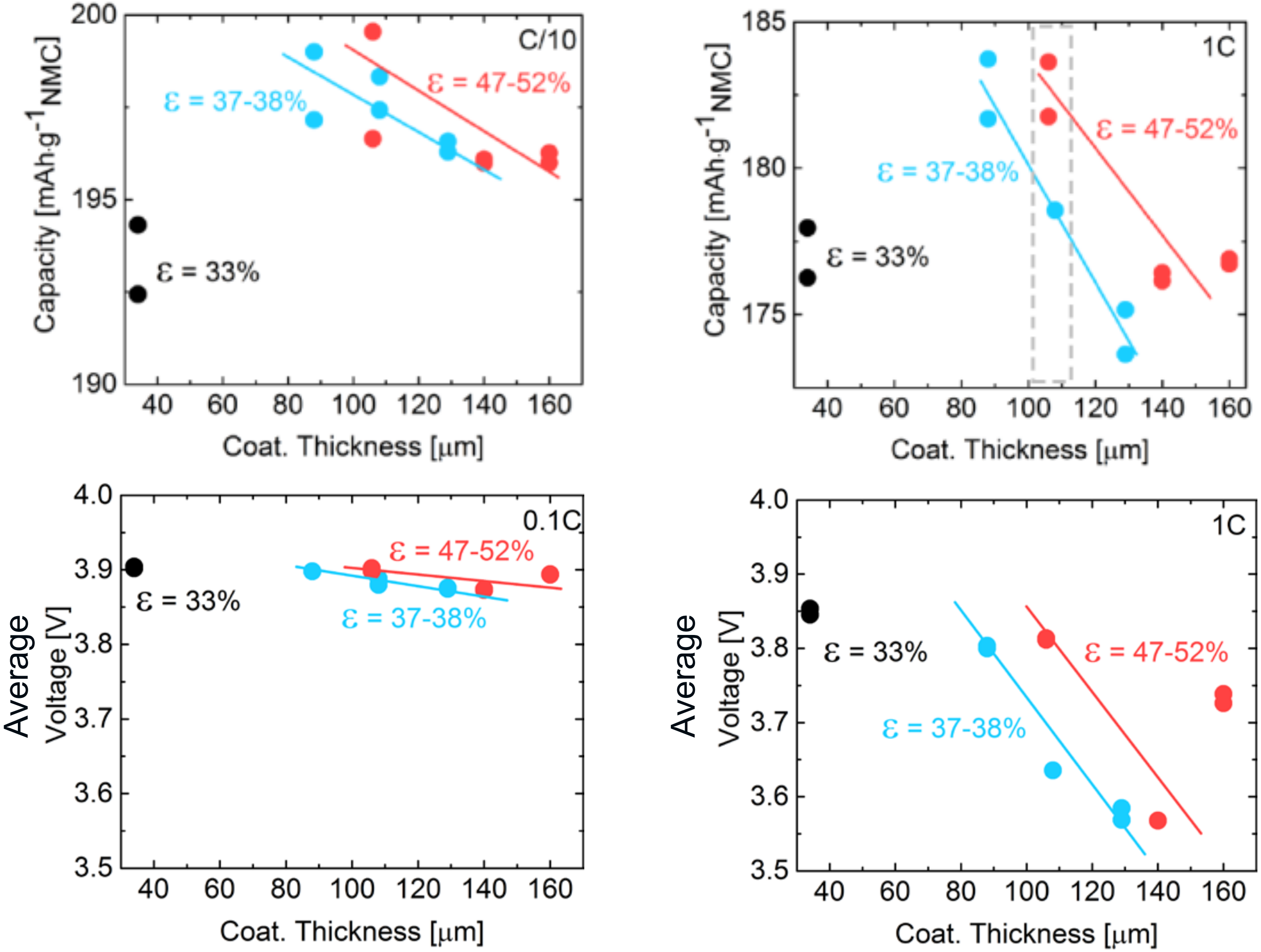
References:

- **ES030** Cell Analysis, Modeling, and Prototyping (CAMP) Research Activities
- **ES252** & **ES253** Enabling High-Energy, High-Voltage Lithium-Ion Cells for Transportation Applications

Electrochemical Characterization of Electrode Library

- Full and half cells (NMC delithiation shown) characterized vs. C-rate

Low rate discharge   High rate discharge



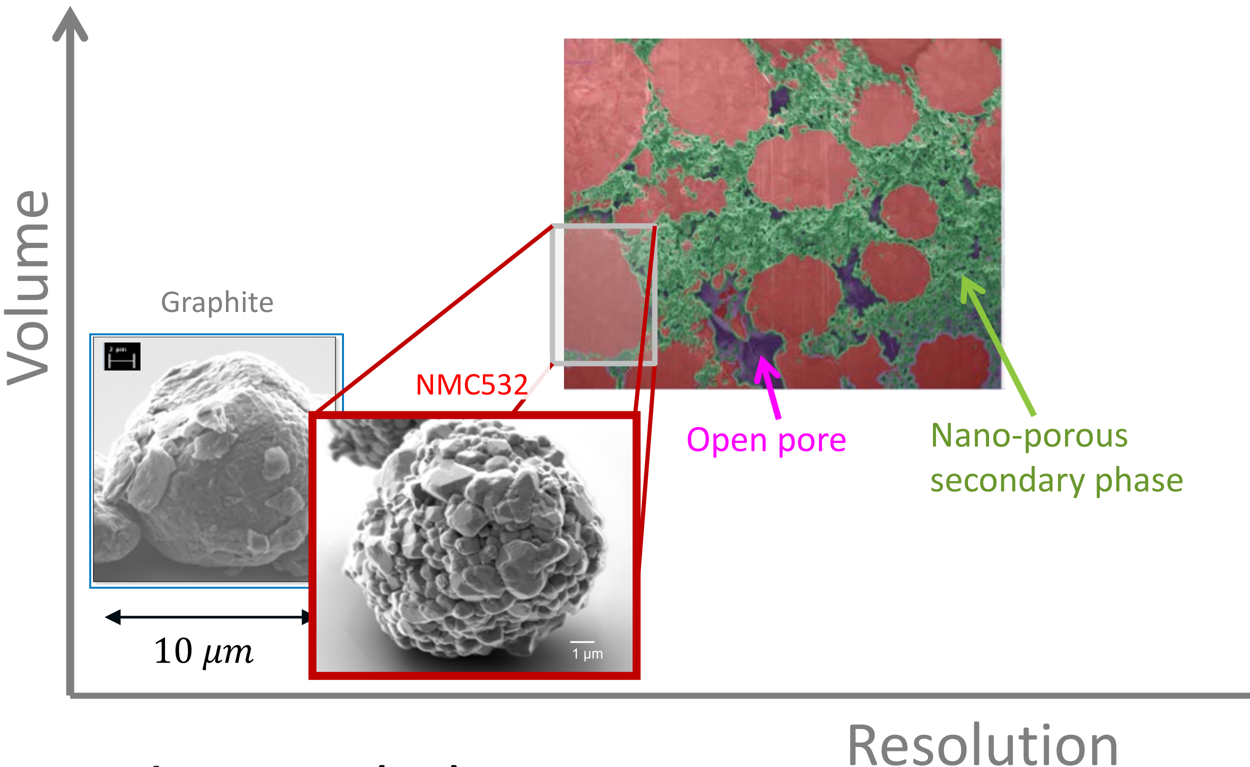
Capacity depends mainly on porosity due to electrolyte transport limitations

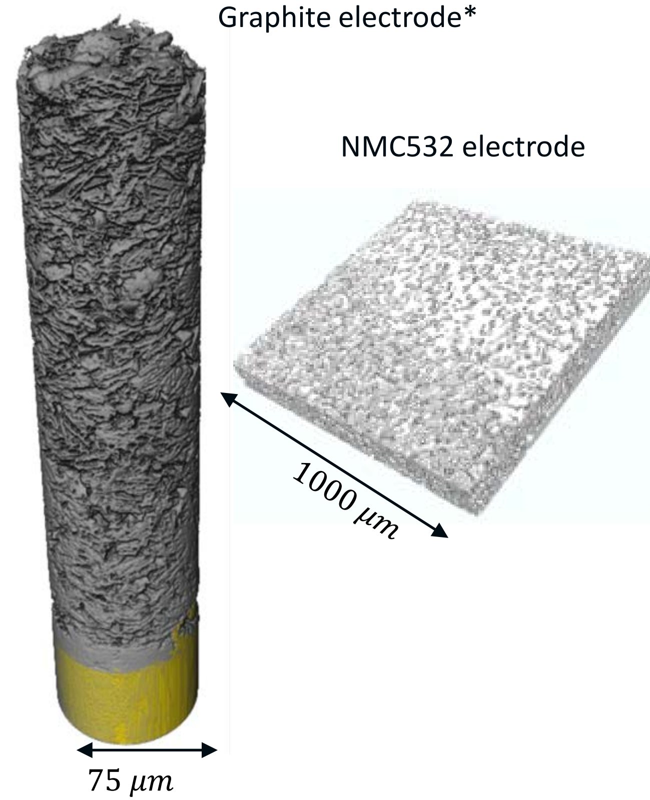
Average voltage drops due to ohmic and polarization losses

NMC: nickel manganese cobalt

Microstructure Characterization Experiments

- **Multiple complementary measurements used to resolve relevant characteristics across length scales**
  - + Analysis and homogenization tools quantify impact
  - + Validate meso-scale electrode design models





*Graphite electrode image courtesy of Paul Shearing & Donal Finegan of UCL. All other images courtesy of Pierre Yao & Daniel Abraham of ANL.

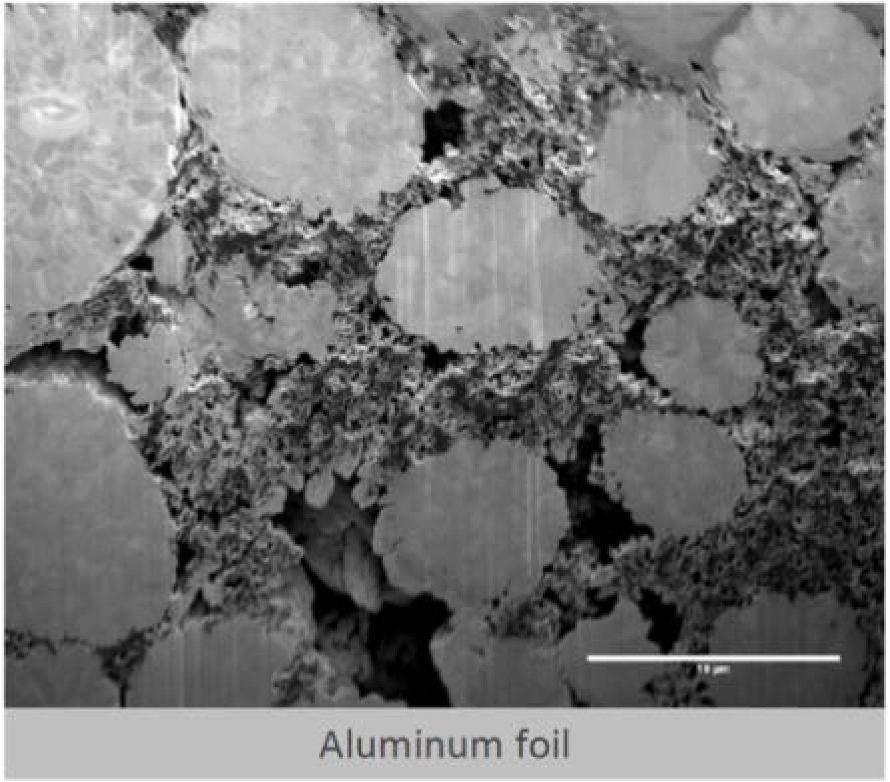
Focused Ion Beam (FIB) – SEM
- Particle surface & morphology
- Secondary phase (conductive additive + binder)

Nano- & Micro-Tomography
- Ionic & electronic tortuous paths

(lacks secondary phase, however)

Meso-scale Simulation – Secondary Phase (1/2)

- Created algorithm for stochastic generation of secondary phase (conductive add. + binder) on active particle matrix
- Virtual geometry generation enables wide design space investigation



FIB-SEM image of NCM 523 electrodes

Figure credit: Koffi (Pierre) Yao and Daniel Abraham, ANL

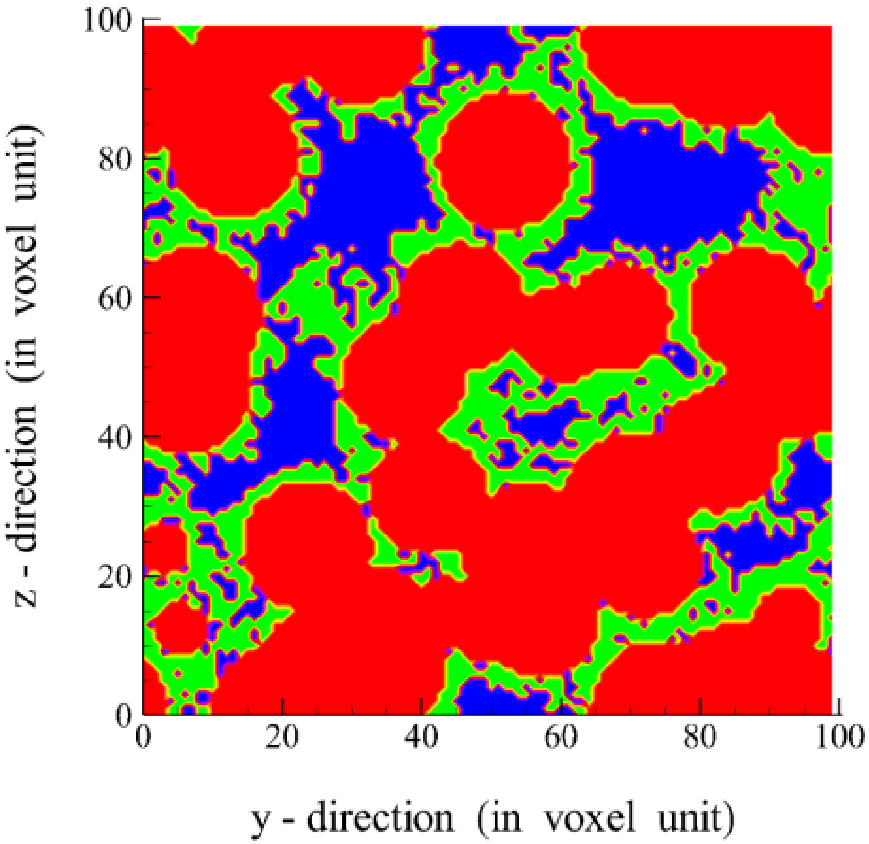
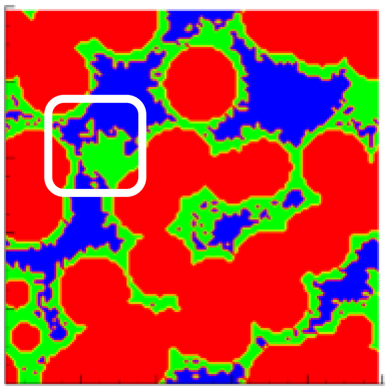


Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

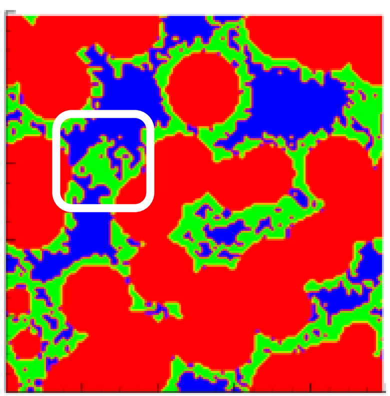
Meso-Scale Modeling – Secondary Phase (2/2)

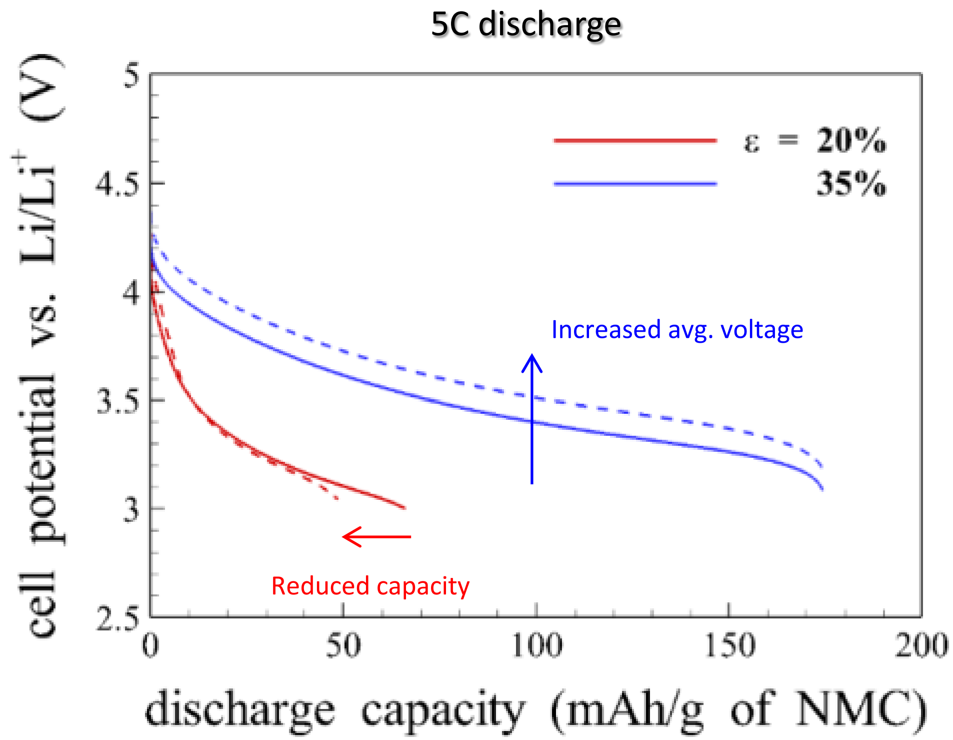
- Secondary phase deposition can take on different morphologies

A) Film-like deposits (solid lines)



B) Finger-like deposits (dashed lines)





Finger-like deposits improve electronic conductivity but introduce additional tortuosity for electrolyte-phase transport

Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Meso-scale Modeling of Electrode Property Relations (1/2)

- Microstructure property relations used in today's macro-homogeneous models hold well in the limit of low solid volume fraction / high porosity…

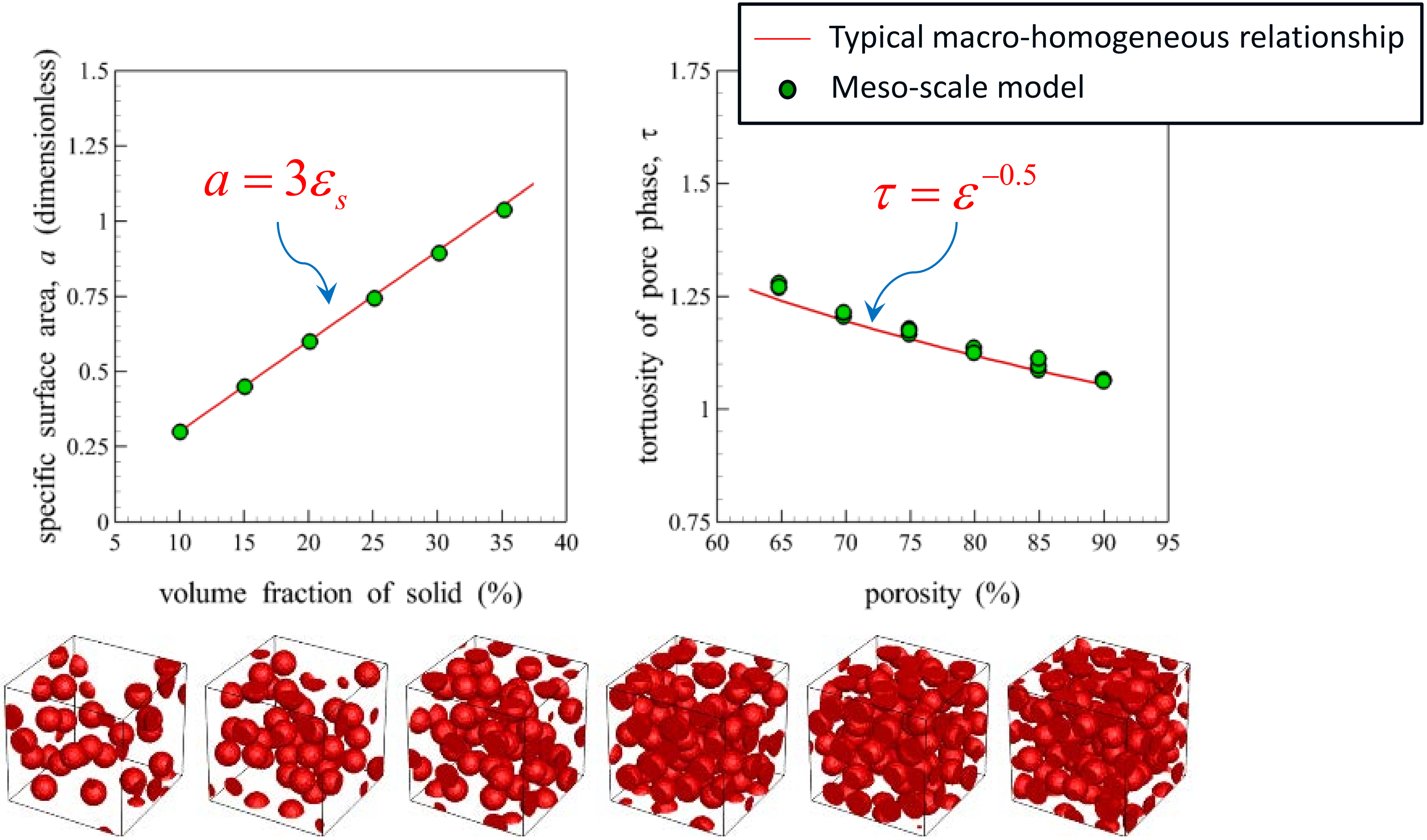


Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Meso-scale Modeling of Electrode Property Relations (2/2)

- … but lose validity for dense electrodes.
- Meso-scale models were used to develop more accurate property relations for dense electrodes across entire electrode design space. To be validated and extended to non-spherical geometries

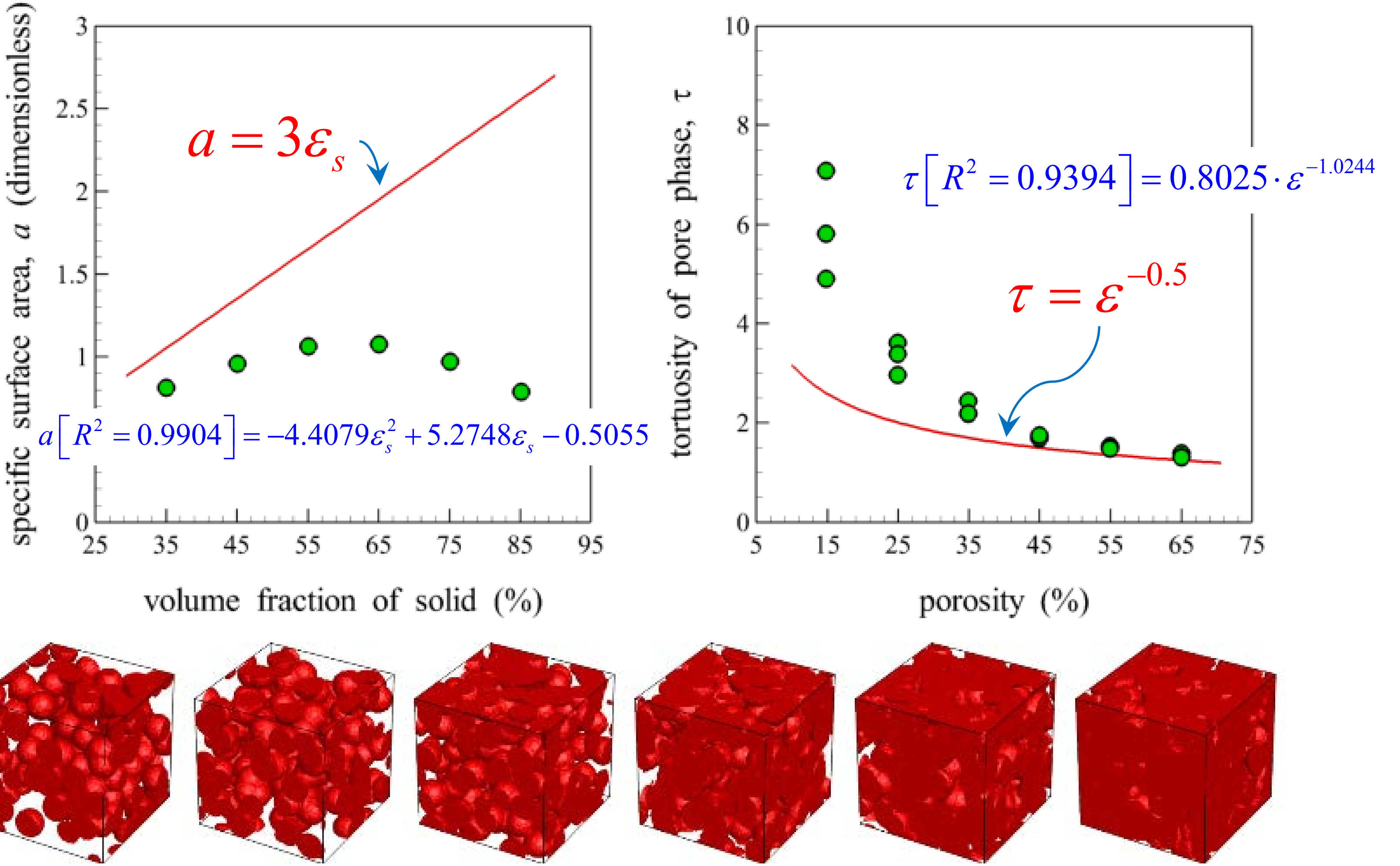


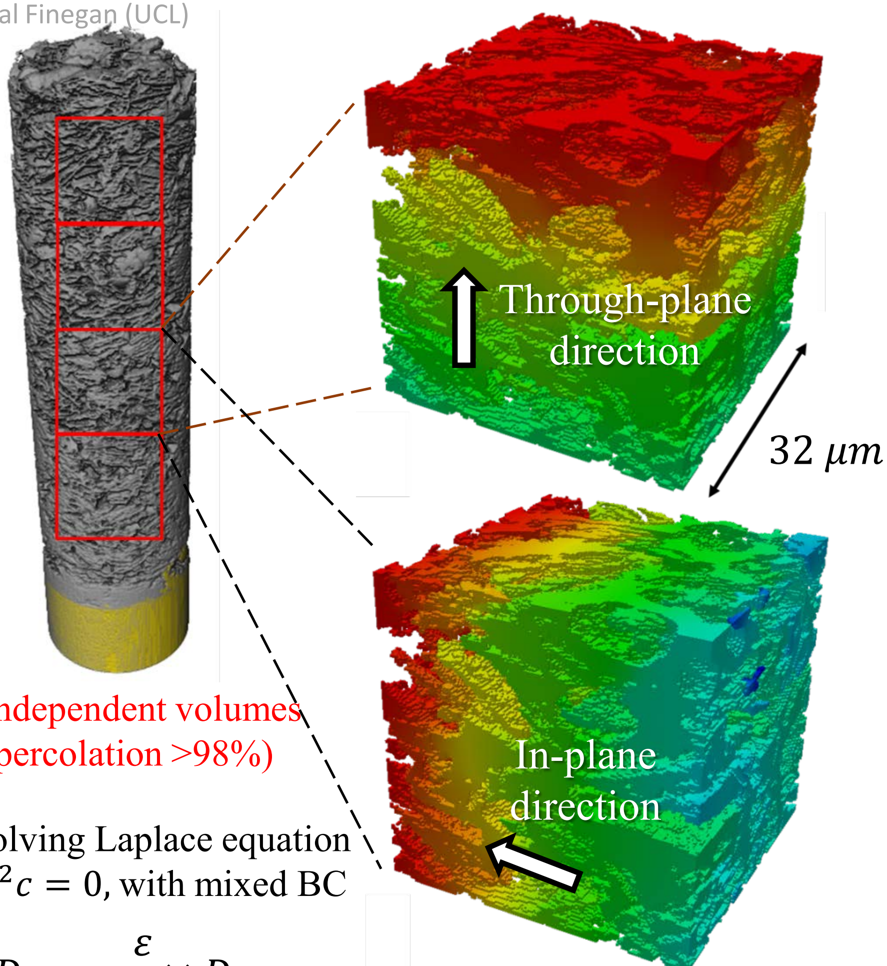
Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Microstructure Analysis – Tortuosity of Ion Transport

- Homogenization calculation reveals (1) high directional impact of non-spherical particles on effective ionic diffusivity and conductivity and (2) calendaring effect on NMC

Graphite geometry, Paul Shearing & Donal Finegan (UCL)

Negative electrode

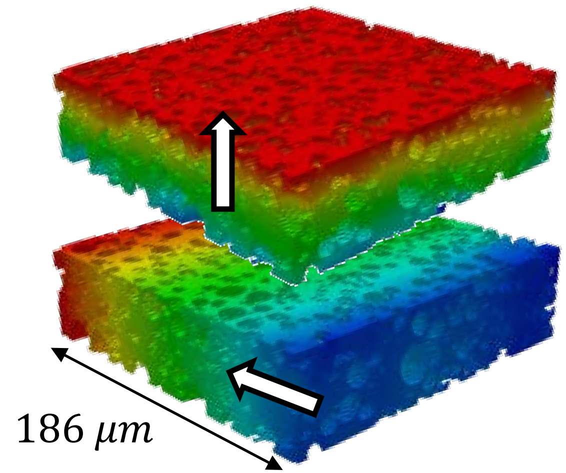


4 Independent volumes (percolation >98%)

Solving Laplace equation $\nabla^2 c = 0$, with mixed BC

$$D_{eff} = \frac{\varepsilon}{\tau} \times D_{dense}$$

Positive electrode (90wt uncalendared)



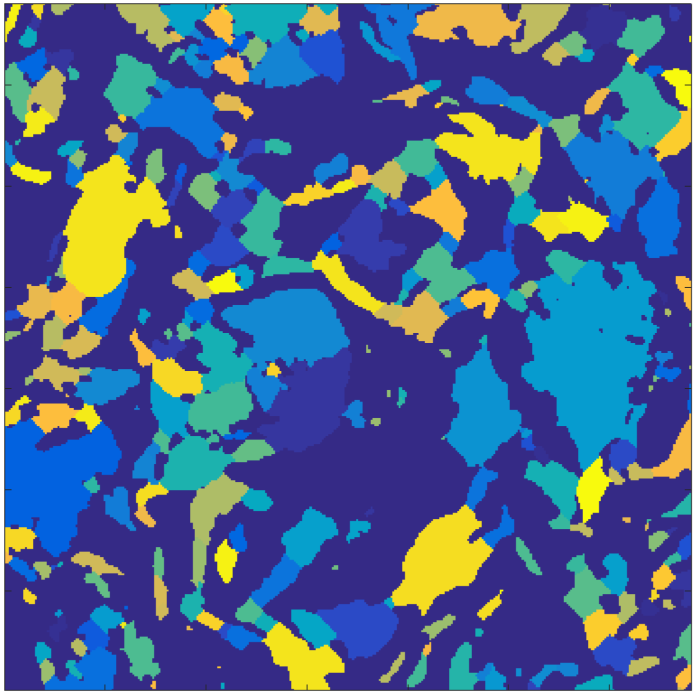
NMC geometry from ETH Zurich (Ebner et al. *Adv. Energy Mater*. **2013**, 3, 845–850)

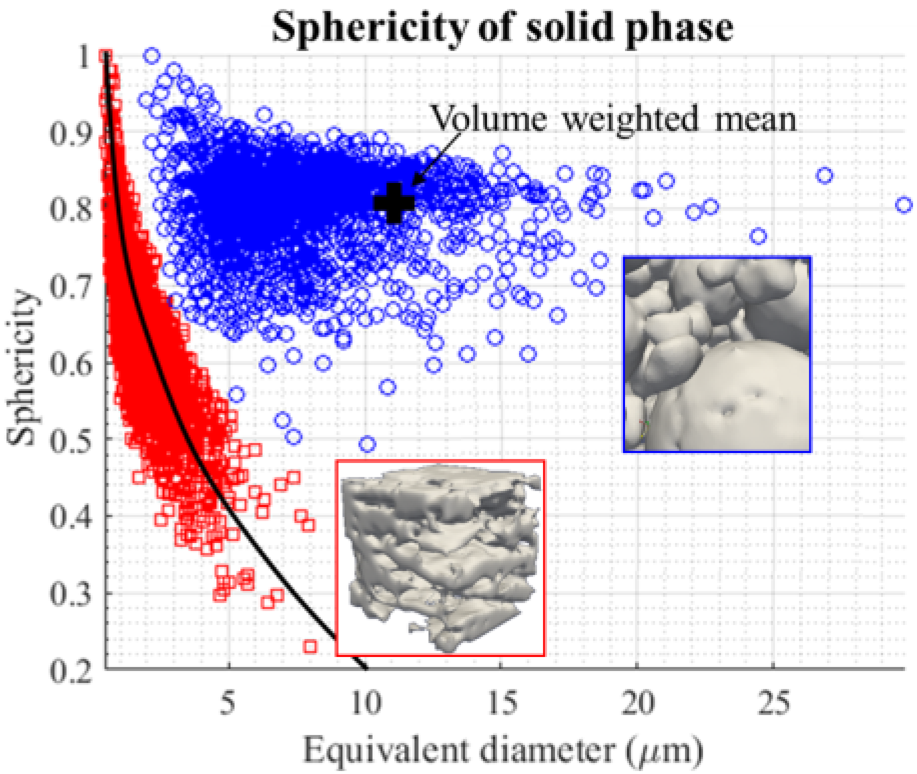
	Negative electrode	Positive electrode UC	Positive electrode C
τ_x (in-plane direction 1)	**1.84**	(90wt) 1.33 (92wt) 1.346 (94wt) 1.426 **Mean: 1.37**	(90wt) 1.477 (92wt) 1.535 (94wt) 1.544 **Mean: 1.52**
τ_y (in-plane direction 2)	**1.85**	(90wt) 1.336 (92wt) 1.343 (94wt) 1.422 **Mean: 1.37**	(90wt) 1.48 (92wt) 1.532 (94wt) 1.574 **Mean: 1.53**
τ_z (through -plane direction)	**3.77**	(90wt) 1.329 (92wt) 1.334 (94wt) 1.415 **Mean: 1.36**	(90wt) 1.620 (92wt) 1.654 (94wt) 1.654 **Mean: 1.64**

Microstructure Analysis – Size and Morphology

- Most models, analyses, and even measurements assume spherical particle shape
- An original discrete particle size distribution algorithm was developed to gain quantitative information of particle statistics w/ no assumption on shape
  - Clear differences between graphite and NCM morphologies
  - Able to quantify elongation and re-alignment of particles due to calendaring effect

Each particle identified with different color





Homogenization Repeated on Different Sub-volumes to Determine Representative Volume Element Size. Multiple Analysis Techniques Compared.

Results on the solid graphite phase

Properties		Typical value*	RVE**
Volume fraction		0.494	$31.8\ \mu m$
Connectivity		99.8 %	$17.6\ \mu m$
Mean diameter	w/ spherical assumption	$0.94\ \mu m$	$30.3\ \mu m$
	w/o spherical assumption	$3.48\ \mu m$	$< 32\ \mu m$
Particle shape sphericit (1=sphere)		0.51	$< 32\ \mu m$
Specific surface area		$2.47\ \mu m^{-1}$	$\sim 40.9\ \mu m$ $(std = 6\%)$
Factor of tortuosity		$\tau_{in-plane} = 1.77$ $\tau_{through-plane} = 3.30$	$> 32\ \mu m$ $(std = 19\%)$

* Different methods are used to calculate the same property. **Methods are not necessarily equivalent (different bias and assumptions)** and thus are **complementary** → mandatory to provide a good overview of the property (i.e., it is risky to rely on a unique method)

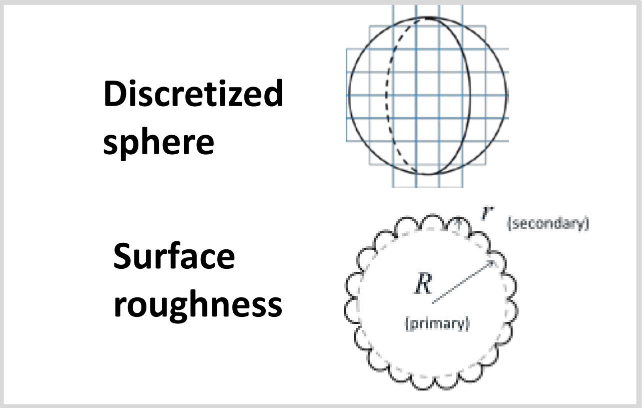
** RVE (representative volume element) is converted in an equivalent cubic volume ($\boldsymbol{a \times a \times a\ \mu m^3}$). It is obtained through statistics analysis of **multiple independent subdomains.**

Differing particle size can result in large variation in prediction of transport limitations for fixed diffusivity

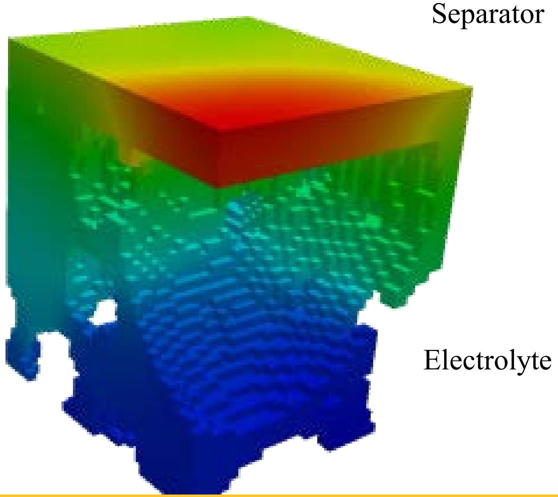
Similar work has been performed for the pore phase, as well as for NMC positive electrode. Additional properties are calculated (e.g., particle size ratio and geometric tortuosity) to achieve a better description of the microstructure.

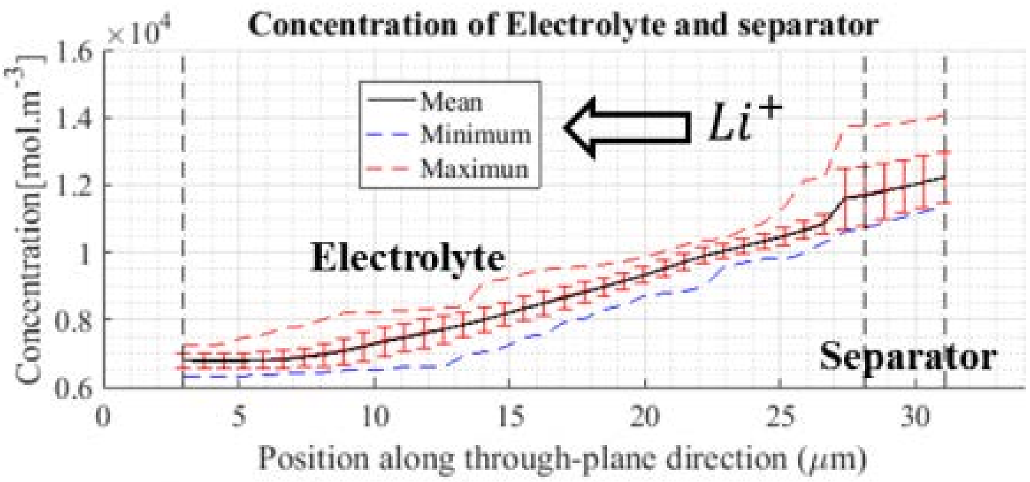
Microstructure Direct Numerical Simulation

- Electrochemical reaction/transport solved using FEniCS open-source finite-element software
- Surface need not be precisely resolved; coarse mesh can be used by applying appropriate area scaling
- Scaling studies demonstrate practical simulation time on NREL's high performance computer, Peregrine
  - 100 x 100 x 100 μm^3 ~ 5 million degrees of freedom



Full physics simulation on microstructure sub-domain





Direct numerical simulation of electrochemistry reveals localized electrochemical phenomena (degradation, under-utilization). Cross-comparison with macro-homogeneous models (Sept. 2017 milestone). Findings to be applied to enhance design and degradation predictive capability of macro-homogeneous models.

Response to Previous Year Reviewers' Comments

- Comment: "It was unclear to this reviewer that the tomographic work has been carefully planned"
  - Response: The team has begun and will continue to carry out multiple measurements to resolve the range of length scales important to the physics of graphite and NMC electrodes of varying recipe
    - FIB-SEM, resolving secondary phase matrix and fine particle features (ANL)
    - Nano-tomography, resolving fine particle features and connectivity (UCL)
    - Micro-tomography, resolving electrode particle/pore connectivity (ANL)

- Comment: "The problem of identifying the minimum representative volume element size has not been addressed"
  - Response: Representative volume element sizes have now been determined for various physical phenomena by studying domain size dependence. RVE methodology is systematically applied for each property. For instance, for the positive electrode (~10-µm particle diameter):
    - Pore phase: RVEs range from $46 \times 46 \times 46\ \mu m^3$ (connectivity) to $116 \times 116 \times 116\ \mu m^3$ (specific surface area & pore size)
    - NMC phase: RVEs range from $65 \times 65 \times 65\ \mu m^3$ (specific surface area & particle size) to $111 \times 111 \times 111\ \mu m^3$ (volume fraction)

Collaboration and Coordination with Other Institutions

NREL (VTO prime)	PI: Kandler Smith Francois Usseglio-Viretta Peter Graf S. Santhanagopalan	• Project lead • Microstructure analysis • Echem. direct numerical simulation • Macro-homogeneous modeling in conjunction with Task 1 - Computational Efficiency
Texas A&M Univ. (non-VTO sub)	PI: Partha Mukherjee Aashutosh Mistry Ankit Verma	• Stochastic reconstruction • Meso-scale modeling • Calculation of microstructure effective properties as function of electrode recipe
Argonne National Lab. (VTO sub)	PI: Daniel Abraham, Koffi (Pierre) Yao, Dennis Dees, Andy Jansen	• Electrode and cell fabrication (CAMP) • Electrochemical characterization • Scanning electron microscopy • Micro-scale computer tomography
Univ. College of London (non-VTO informal collaborator)	PI: Paul Shearing Donal Finegan	• Nano-scale computed tomography

Remaining Challenges and Barriers

Obtaining and validating a realistic physical description of all factors of electrode design in a toolset practical for application in the battery design cycle

- Stochastic reconstruction capturing interfacial heterogeneities
- Homogenization capturing tortuosity of nano-porous secondary phase
- Direct measurement of effective properties (e.g., electronic & ionic conductivity) to
  - Validate meso-scale models
  - Validate tortuosity homogenization calculations
- Large number of measurements to validate all length scales of problem, ranging from secondary phase nano-porosity (<100 nm) to electrode-scale effective properties (~100 μm)
- Ensuring representative volumes are achieved in all measurements and simulation results

Proposed Future Research

- Complete tomographic characterization of graphite and NMC532 electrodes from CAMP electrode library
- Measure electrode effective ionic and electronic conductivity
- Extend meso-scale electrode design model to non-spherical active material morphology and incorporate relevant aspects of calendaring
- Validate meso-scale model predictions for electrode designs of varying thickness, porosity and composition
- Scale microstructure DNS model to full electrode domain RVE size using high-performance computing
- Validate microstructure DNS model versus electrochemical data and macro-homogeneous models
- In collaboration with CAMP and other prototyping facilities, apply validated model suite to propose thick electrode designs that optimize energy density while avoiding performance and reliability limitations.

* Proposed future work is subject to change based on funding levels

Summary

- Completed electrochemical characterization of graphite and NMC532 electrodes from CAMP electrode library in half- and full-cell configurations
- Initiated microstructure characterization through FIB-SEM, nano- and micro-tomography
- Developed approach for stochastic reconstruction of secondary phase for meso-scale modeling
- Applied meso-scale model to map effective properties of NMC composite electrode versus electrode recipe
- Developed toolset for homogenization and microstructure analysis
    - Original discrete particle algorithm capturing non-spherical morphology
- Developed microstructure DNS model and initiated scale-up to HPC

Demonstrated approach for comprehensive modeling toolset for electrode microstructure design with scale-up to CAEBAT cell and pack models. To be further extended and validated in remaining 1.5 years of project.

Acknowledgements

- We appreciate support and funding provided by Vehicle Technologies Office at the U.S. Department of Energy
  - Brian Cunningham
  - David Howell
  - Samuel Gillard

- Also, thanks to collaborators
  - Bryant Polzin, Stephen Trask – ANL CAMP Facility
  - Donal Finegan, Paul Shearing – UCL